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The University of Chicago
Founded by John D. Rockefeller

On the Oxidation of *d*-Glucose in Alkaline Solution by Air as well as by Hydrogen Peroxide

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE
SCHOOL OF SCIENCE IN CANDIDACY FOR THE
DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

By JOHN WILLIAM EDWARD GLATTFELD

EASTON, PA.:
PRESS OF THE ESCHENBACH PRINTING CO.
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On the Oxidation of *d*-Glucose in Alkaline Solution by Air as well as by Hydrogen Peroxide

The oxidation of *d*-glucose in approximately half normal potassium hydroxide solution (9 molecules) by means of hydrogen peroxide has been studied in this laboratory by Spoehr,[1] who found that four oxidation products—namely, small amounts of carbon dioxide (3.51 per cent.), glycollic acid and a new hexonic acid, $C_6H_{12}O_7$, α-hydroxymethyl-*d*-arabonic acid, besides very large amounts of formic acid (65.3 per cent.)—are formed.

Preliminary experiments by Nef had convinced him that Spoehr, in carrying out the very difficult separations by means of alkaloidal salts, must have overlooked the presence of *dl*-glyceric acid and of isomeric trihydroxybutyric acids which are also formed in this oxidation process; and since, furthermore, Nef has recently succeeded in finding a perfectly general method for oxidizing all sugars in very dilute alkaline solutions at low temperatures (40°) with air *without the simultaneous formation of saccharinic acids*, it was now possible to show also by experiment that *d*-glucose, when oxidized in alkaline solution by air, gives exactly the same oxidation products as when hydrogen peroxide is used. The problem therefore assigned to me by Dr. Nef was to determine especially the nature of all the nonvolatile hydroxy acids formed from *d*-glucose in alkaline solution by air as well as by hydrogen peroxide.

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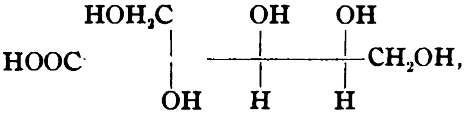
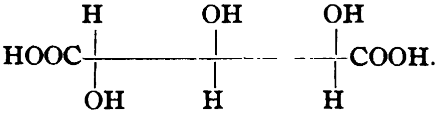
[1] Am. Chem. J., 42, 233–245.

The new hexonic acid considered by Spoehr to be α-hydroxymethyl-*d*-arabonic acid,



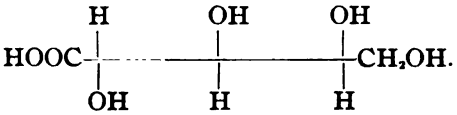
$$\mathrm{HOOC}\overset{\mathrm{HOH_2C}}{\underset{\mathrm{OH}}{|}}\;-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{|}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{|}}-\mathrm{CH_2OH},$$

was obtained by him in the form of a thick viscous lactone gum possessing a specific rotation of 72°.5, and he had apparently established its constitution as named by an analysis of its well-crystallized calcium salt, and of its phenylhydrazide, as well as by its oxidation, with loss of carbon dioxide, to *d*-trihydroxyglutaric acid,



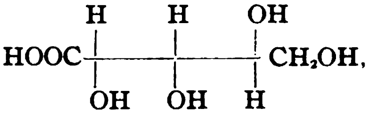
$$\mathrm{HOOC}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{|}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{|}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{|}}-\mathrm{COOH}.$$

I succeeded in obtaining Spoehr's acid in the form of its crystallized γ-lactone melting at 96°–98° and have made an exhaustive study of its crystalline derivatives; it finally became perfectly apparent that the acid was not a new hexonic acid but a pentonic acid identical with Ruff's *d*-arabonic acid,



$$\mathrm{HOOC}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{|}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{|}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{|}}-\mathrm{CH_2OH}.$$

In an exactly similar way Dr. Nef has recently proved that Lucas' so-called new α-hydroxymethyl-*d*-lyxonic lactone,[1] which is obtained in large quantities by oxidizing *d*-galactose in dilute sodium hydroxide solution by air, is identical with the γ-lactone of *d*-lyxonic acid,



$$\mathrm{HOOC}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{|}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{|}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{|}}-\mathrm{CH_2OH},$$

i. e., an optically active pentonic acid is formed.

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[1] Ann. Chem. (Liebig), **376**, 55, footnote.

We have therefore here at last the proof sought for for over nine years past by Nef[1] that all hexose sugars in the form of 1,2-hexosedienols,

$$\mathrm{HOCH = C(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).CH_2OH},$$

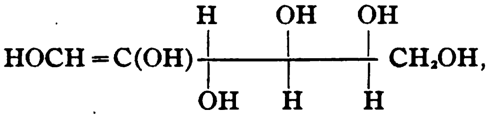
dissociate into hydroxymethylene and various methylenenols of pentose sugars; and since previous experiments by Nef prove very sharply that hexose sugars in the form of 2,3-hexosedienols,

$$\mathrm{HOCH_2.C(OH) = C(OH).\overset{*}{C}H(OH).\overset{*}{C}H(OH).CH_2OH},$$

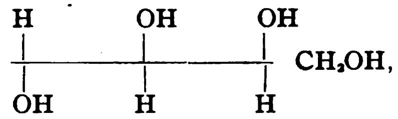
and 3,4-hexosedienols,

$$\mathrm{HOCH_2.\overset{*}{C}H(OH).C(OH) = C(OH).\overset{*}{C}H(OH).CH_2OH},$$

dissociate into diose and isomeric tetrose sugars as well as into two molecules of glyceraldehydemethylenenol, it is now certain that every hexose sugar in alkaline hydroxide medium, besides giving a mixture of six sugars of the corresponding series,[2] splits spontaneously into a mixture of various sugars containing one, two, three, four and five carbon atoms, $(CH_2O)_x$. The 1,2-*d*-glucosedienol,


$$\mathrm{HOCH{=}C(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

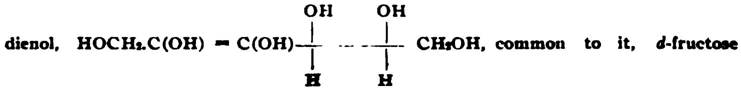
common to *d*-glucose, *d*-mannose and *d*-fructose, obviously splits into hydroxymethylene, $>$CHOH, and the methylenenol of *d*-arabinose, $>$C(OH)


$$>\mathrm{C(OH)}-\underset{\mathrm{OH}}{\overset{\mathrm{H}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

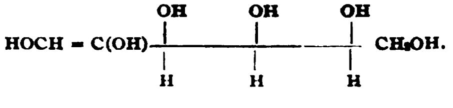
---

[1] Ann. Chem. (Liebig), **357**, 259; **376**, 52.

[2] **d-Allose and d-latose are *not* present as members of the d-glucose series [cf. *Ann.* Chem. (Liebig), 357, 294; 376, 87] because d-pseudofructose gives only a 2,3-d-glucosedienol,**

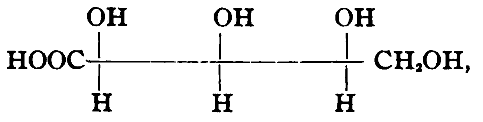

$$\mathrm{HOCH_2.C(OH) = C(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH},$$

common to it, d-fructose and α- and β-d-galtose, and not a β-1,2-d-glucosedienol,


$$\mathrm{HOCH = C(OH)}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\underset{\mathrm{H}}{\overset{\mathrm{OH}}{|}}-\mathrm{CH_2OH}.$$

J. U. Nef.

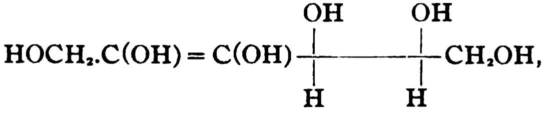
which then mainly takes up oxygen to give *d*-arabonic acid; at the same time it is very probable that some *d*-ribonic acid,



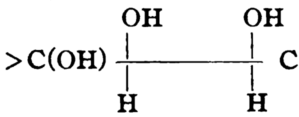
$$\mathrm{HOOC}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\!\!-\!\!-\!\!-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\!\!-\!\!-\!\!-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\mathrm{CH_2OH},$$

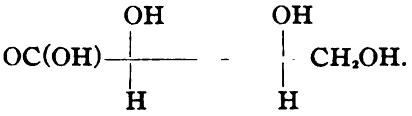
is also formed, but I was unable to establish this experimentally (see below).

The 2,3-*d*-glucosedienol,



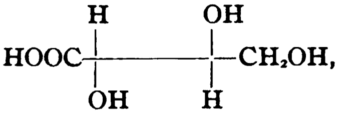
$$\mathrm{HOCH_2.C(OH) = C(OH)}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\!\!-\!\!-\!\!-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\mathrm{CH_2OH},$$

similarly splits into the methylenenols of diose, $\mathrm{HOCH_2.C(OH)} <$, and of *d*-erythrose,  $>\mathrm{C(OH)}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\!\!-\!\!-\!\!-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\mathrm{CH_2OH}$, which should therefore take up oxygen to give *d*-erythronic acid,



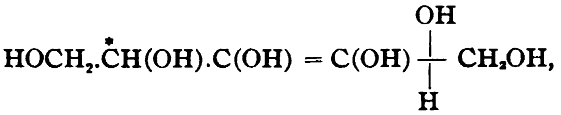
$$\mathrm{OC(OH)}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\!\!-\!\!-\!\!-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\mathrm{CH_2OH}.$$

This was in fact the *chief optically active trihydroxybutyric acid* found by me among the oxidation products of *d*-glucose with air as well as with hydrogen peroxide; at the same time a very small amount of optically active *l*-threonic acid,



$$\mathrm{HOOC}\overset{\mathrm{H}}{\underset{\mathrm{OH}}{+}}\!\!-\!\!-\!\!-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\mathrm{CH_2OH},$$

is also unquestionably formed. The 3,4-*d*-glucosedienol,



$$\mathrm{HOCH_2.\overset{*}{C}H(OH).C(OH) = C(OH)}\overset{\mathrm{OH}}{\underset{\mathrm{H}}{+}}\mathrm{CH_2OH},$$

obviously splits spontaneously as soon as formed into two molecules of glyceraldehydemethylenenol,

$$2\mathrm{HOCH_2.CH(OH).C(OH)} <,$$

which naturally takes up oxygen to give *dl*-glyceric acid, hence this acid was found by me as an oxidation product under the conditions named. In addition, glycollic acid and especially large amounts of formic acid (65.2 per cent. and 14.8 per cent., respectively, with hydrogen peroxide and air) are obtained as oxidation products; these are formed mainly through the direct oxidation of hydroxymethylene, $>$CHOH, and of diosemethylenenol, $HOCH_2C(OH)<$.

Especially noteworthy is the fact that *none* of the six-carbon-atom sugars originally present in the alkaline solution—*d*-glucose, *d*-mannose, *d*-fructose, *d*-pseudofructose and α- and β-*d*-glutose (3-ketohexoses)—actually oxidize to their corresponding hexonic acids. This apparently only happens when Fehling's solution is used.[1] It is still possible that small quantities of *d*-mannonic and *d*-gluconic acids are formed when *d*-glucose (or any other of the six components of the *d*-glucose series) is oxidized in alkaline solution by air or hydrogen peroxide, but I was unable to establish their presence by experiment.

EXPERIMENTAL PART

I. The Action of Hydrogen Peroxide on d-*Glucose in Alkaline Solution*

In order to obtain as much nonvolatile hydroxy acid gum as possible, 75 grams of *d*-glucose were dissolved in two liters of cold three per cent. hydrogen peroxide and six equivalents of concentrated sodium hydroxide solution (102 grams of ninety-eight per cent. sodium hydroxide in 240 cc. water) were then slowly added in approximately equal portions, one equivalent immediately and the others at the end of 5, 9, 23, 27 and 32 hours, respectively. One hundred cc. more hydrogen peroxide were added at the end of 29 hours and when all the alkali had been introduced—at the end of 32 hours—465 cc. more hydrogen peroxide were added, so that the total volume of the solution rose to about three liters. The mixture was then allowed to stand 39 hours longer at ordinary temperature, when the test for sugar had become very faint, whereas the solution still gave—as throughout every stage in the oxidation process—a strong test for hydrogen peroxide.

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[1] Cf. Nef: Ann. Chem. (Liebig), **357**, 259–286.

Four such portions of seventy-five grams of *d*-glucose were worked up simultaneously, as well as another portion of 50 grams of *d*-glucose in 1500 cc. three per cent. hydrogen peroxide, to which, however, the six equivalents of sodium hydroxide in a small amount of cold water had been added in portions in the course of five days instead of 32 hours as in the other four cases.

At the end of seventy-one hours each of the four solutions was concentrated by distillation at 50° under 40 mm. pressure to about 800 cc. A test for sugar at this point showed none to be present. The solutions were then extracted twice with ether in order to remove small amounts of aniline formed by the hydrolysis of acetanilide which was present in very small amounts in the commercial hydrogen peroxide used. They were then acidified with concentrated hydrochloric acid. Twice the amount necessary to neutralize the alkali used was added. On distilling to a small volume at 60° under 30 mm. pressure, large amounts of sodium chloride had separated out. About two liters of 95 per cent. alcohol was now added to the mixture. The sodium chloride was filtered off and washed thoroughly with 95 per cent. alcohol. The filtrates were then distilled off completely at 60° under 30 mm. pressure and the residue was thoroughly extracted with absolute alcohol. At this stage the corresponding absolute alcohol extract obtained from the above-mentioned oxidation of 50 grams of *d*-glucose was combined with those obtained from 300 grams *d*-glucose as just stated, and the alcohol was then removed by distillation at 60° under 20 mm. pressure, giving thus a total of 83 grams crude brown nonvolatile gums, from 350 grams *d*-glucose, which still contained a very small amount of sodium chloride.

These gums were now resolved by two successive digestions with one liter of ethyl acetate into two soluble fractions:[1] 39 grams with $[\alpha]_D^{20}$ 33°.97 and 6.5 grams with $[\alpha]_D^{20}$ 47°.08, after freeing from ethyl acetate, etc., by sweeping over with water at 80° under 20 mm. pressure. These fractions were again united and extracted four times with one liter of ether and thus a total of 17.45 grams soluble gums, *A*, with $[\alpha]_D^{20}$ 23°.78, was obtained, leaving 25.5 grams gums, *B*, undissolved. The portion of the original 83 grams gums left undissolved by ethyl acetate was found to weigh 31 grams, gum *C*, with $[\alpha]_D^{20}$ 44°.35. Since *d*-arabonic acid gives a very difficultly soluble phenylhydrazide, and it was obviously not possible to separate the nonvolatile hydroxy acids to any appreciable degree by fractional solution in solvents, I decided to treat the gums *A*, *B* and *C* with phenylhydrazine. This was invariably done by mixing the gums with a volume each of phenylhydrazine and absolute alcohol equal to the weight of the gum taken, warming gently and stirring until a homogeneous mixture resulted. The crystalline hydrazide separated out completely in the course of 24 hours' standing at ordinary temperature, and was then filtered off and washed until snow-white with absolute alcohol. The gummy hydrazides left in the alcoholic filtrates were freed from alcohol by distillation under 20 mm. pressure in a bath kept at 40°–50°, and then freed from the excess of phenylhydrazine by threefold extraction in aqueous solution with ether. On removal of the water by distillation under reduced pressure, and dissolving the residue in eight parts of absolute alcohol, usually a fair amount more of crystalline hydrazide separated out. In this way I obtained from the above-mentioned three gums a total of 72.15 grams of acid hydrazides melting from 195° to 209°, as follows: Gum *A*, 17.45 grams, gave 8.8 grams crystals melting from 205° to 209°; Gum *B*, 25.5 grams, gave 25.95 grams crystals melting from 195°–204°; Gum *C*, 31 grams, gave 30.1 grams crystals melting from 195°–200°. The combined alcoholic filtrates, treated as stated above, gave 54 grams of gummy hydrazides which, dissolved in 400 cc. absolute alcohol, gave 7.3 grams more of crystals melting at 195°, and the gummy hydrazides left in the filtrate, 45 grams, hydrolyzed 7 hours on a boiling water bath with 45 grams barium hydroxide, 45 cc. water, etc. (see below), gave back 19 grams of nonvolatile hydroxy acids (see below) which were found to be optically inactive.

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[1] All the optical determinations in the entire course of this work were made in approximately 4 per cent. aqueous solution.

The Conversion of the Crude d-*Arabonic Phenylhydrazide into* γ-d-*Arabonic Lactone*

The 72.15 grams of crude *d*-arabonic phenylhydrazide obtained as just described were now hydrolyzed by heating 7 hours on a boiling water bath with 72 grams of crystallized barium hydroxide and 72 cc. water, taking care to shake from time to time. Much water was then added and the solution was filtered; the solids on the filter paper were then washed free of phenylhydrazine with ether and the filtrate also extracted five times with ether in order to remove the phenylhydrazine. The extracted solids and filtrate were then united and the barium precipitated in the usual manner, taking care to leave a trace of barium finally in the clear filtrate, which was then digested with charcoal. The crude *d*-arabonic lactone gum obtained after the customary removal of the water and extraction of the residue with absolute alcohol weighed 34 grams, $[\alpha]_D^{20}$ 60°.73, whereas the amount demanded by theory is 42 grams.

Nef has repeatedly emphasized[1] the fact that it is impossible to convert any polyatomic tetronic, pentonic or hexonic acid quantitatively into its γ-lactone. He has recently succeeded in isolating the pure β and γ monomolecular lactones of *d*-mannonic and *d*-gluconic acid.[2] *d*-Arabonic acid must therefore also give two lactones and this explains, in part at least, why I did not succeed in transforming the 34 grams of crude lactone gums quantitatively into the pure γ-lactone. Since, according to Nef's observations, the γ-lactone is invariably formed in larger ratio at higher temperatures, the method of procedure to obtain the γ-lactone is as follows: The crude lactone is first extracted with hot ethyl acetate and as much crystallized lactone is then obtained from the clear filtrate as possible by concentration, seeding, etc. As soon as the ethyl acetate solutions give no more crystals, the solvent is removed by distillation under reduced pressure and the residual β,γ-lactone mixture then heated in concentrated aqueous solution for 5 hours on a boiling water bath. The water is then removed by distillation at high pressure and temperature, 80°–100°, and the gum then finally kept at 100° for some time under a pressure of 20 mm. This residue will then give more γ-lactone crystals with ethyl acetate, etc.

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[1] Ann. Chem. (Liebig), **357**, 236.

[2] Soon to be published as a thesis by O. F. Hedenburg in Am. Chem. J.

I succeeded in this way in obtaining a total of 23.18 grams crude γ-*d*-arabonic lactone crystals, which melted at about 96°, from the above-mentioned 34 grams of crude lactone mixture; and in addition 9 grams of gummy lactones, $[\alpha]_D^{20}$ 52.08°, were obtained from the ethyl acetate filtrates which were treated with brucine as described further on.

Pure γ-d-*Arabonic Lactone.*—On decolorizing with animal charcoal the aqueous solution of 11 grams crude γ-*d*-arabonic lactone crystals which consisted in part of the 23.18 grams mentioned above and in part of the 4.49 grams of similar γ-*d*-arabonic lactone crystals obtained in the air experiment, distilling the solution at 100° under 20 mm. pressure, taking up the residual gum in ethyl acetate and concentrating this solution under reduced pressure, I obtained in all 8.23 grams of beautiful, transparent, hard, measurable crystals melting at 96° to 98°. Ruff[1] gives the melting point of *d*-arabonic lactone as 97°–98° and its specific rotation as 73°.73 (in 10 per cent. concentration). Since it was not possible to determine by analysis whether a pentonic or a hexonic lactone was present, this was determined in favor of *d*-arabonic lactone by four independent titrations by two observers, Dr. Upson and myself, with 0.1 N alkali. Furthermore, I obtained a specific rotation of 68°.94 and 69°.68, respectively, for the crystals in four per cent. aqueous solution as follows:

(*a*) 0.6009 gram substance and 14.6303 grams water gave α in a 1 dcm. tube = 2°.75; and

(*b*) 0.4179 gram substance and 10.6952 grams water gave α in a 1 dcm. tube = 2°.65.

The analysis of 0.2149 gram substance gave 0.1054 gram H_2O and 0.3183 gram CO_2.

	Calculated for $C_5H_8O_5$	Found
C	40.54	40.40
H	5.40	5.49

---

[1] Ber. d. chem. Ges., **32**, 557.

Titration of the Lactone.—(1) 0.5298 gram lactone required 34.2 cc. 0.1 N sodium hydroxide for neutralization; the calculated value for $C_5H_8O_5$ is 35.8 cc. and for $C_6H_{10}O_6$, 29.78 cc.

(2) 0.4179 gram lactone required 26.3 cc. 0.1 N sodium hydroxide; calculated for C_5 lactone 28.24 cc. and for C_6 lactone 23.48 cc.

(3) 0.6009 gram lactone required 40.3 cc. 0.1 N sodium hydroxide; calculated for C_5 is 40.6 cc. and for C_6 is 33.76 cc.

(4) 0.603 gram lactone required 41.0 cc. 0.1 N sodium hydroxide (Upson); calculated for C_5 lactone is 40.75 cc. and for C_6 33.88 cc.

d-Arabonic lactone was therefore unquestionably present and this was further established by the analysis of the acid hydrazide and the calcium salt.

d-*Arabonic Phenylhydrazide.*—This compound was formed quantitatively by mixing 1 gram of pure lactone crystals with one volume each of phenylhydrazine and absolute alcohol. The crystals, which had separated out completely after 24 hours, were washed until snow-white with absolute alcohol and melted, after drying on a clay plate and *in vacuo* over sulphuric acid, between 213° and 214°. Ruff[1] gives the melting point of *d*-arabonic phenylhydrazide as 214°. The melting point of the antipode, *l*-arabonic phenylhydrazide, is likewise 214°, and its specific rotation in two per cent. aqueous solution has been determined by Nef as 14°.94, while Spoehr[2] gives —13°.9 as the specific rotation of the *d*-arabonic hydrazide in two per cent. aqueous solution. The analysis of my product shows very clearly that a pentonic and not a hexonic phenylhydrazide is at hand.

0.2852 gram substance gave 0.5384 gram CO_2 and 0.1612 gram H_2O.

0.2292 gram substance gave 22.4 cc. N_2 at 22°.3 C. under 729.9 mm. pressure.

	Calculated for		Found
	$C_{11}H_{16}O_5N_2$	$C_{12}H_{18}O_6N_2$	
C	51.54	50.35	51.49
H	6.30	6.29	6.32
N	10.94	9.79	10.86

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[1] *Loc. cit.*

[2] Am. Chem. J., **43**, 240.

Calcium d-*Arabonate,* $(C_5H_9O_6)_2Ca.5H_2O$.—The crystallized calcium salt here studied was made from a gummy lactone obtained from crude *d*-arabonic brucine crystals (melting point, vacuum dried, 170°–176°) by hydrolysis. After the calcium determinations given below had been made the rest of this calcium salt—11.78 grams—was converted by the usual method into 6.56 grams gummy lactone; 5.29 grams of this gum gave with ethyl acetate, etc., 3.87 grams crystallized γ-*d*-arabonic lactone melting about 95° and with $[\alpha]_D^{20}$ 68°.65.

Three determinations of the calcium content of this salt were made. According to Ruff[1] this salt crystallizes with 5 molecules of water—the same is also true of its antipode—which cannot be removed *in vacuo* over sulphuric acid.

I. 0.2380 gram vacuum-dried salt gave 0.0292 gram CaO.
II. 0.2312 gram salt gave 0.0284 gram CaO.
III. 0.2730 gram salt gave 0.0338 gram CaO.

	Calculated for $(C_5H_{10}O_6)_2Ca.5H_2O$	Found I	 II	 III
Ca	8.71	8.77	8.78	8.85

The specific rotation of this salt, calculated for the anhydrous salt, was found to be, in agreement with Spoehr,[2] —3°.19 : 0.5656 gram salt dissolved in 13.4431 grams water gave α in a 1 dcm. tube = —0°.105, whence $[\alpha]_D^{20}$ for the hydrated salt is —2°.57 and for the anhydrous salt —3°.19.

Cinchonine d-*Arabonate.*—On heating an aqueous solution of 1 gram crude γ-lactone crystals for 4 hours on a boiling water bath with an excess of cinchonine, filtering off the undissolved alkaloid and distilling the clear solution at 70° under 20 mm. pressure, 2.50 grams of crude salt were obtained which required 30 cc. of hot absolute alcohol for solution. The clear filtrate deposited 1.08 grams of salt in the form of hard, radiating needles, melting between 178° and 180°, and possessing $[\alpha]_D^{20}$ 120°.3, *i. e.*, 0.405 gram salt and 9.9887 grams water gave α in a 1 dcm. tube = 4°.74.

Since Nef[3] has shown that cinchonine *l*-arabonate is a gummy salt very soluble in cold absolute alcohol—an observation which I have confirmed—it is evident that *dl*-arabonic lactone can easily be resolved into its optical components by means of cinchonine. It follows also from this that the cinchonine *d*-gluconate obtained by Nef in his oxidation experiments with *d*-glucose, *d*-mannose, and *d*-fructose and Fehling's solution[1] must have contained cinchonine *d*-arabonate which—unlike its antipode—is also very difficultly soluble in absolute alcohol. Dr. Nef informs me that he feels certain that this was the case because the melting point of the cinchonine *d*-gluconate obtained by him in these experiments was not sharp (189°) but ranged from 170° to 187°. Furthermore, he noticed especially that on setting free the *d*-gluconic gum from this salt mixture he had great difficulty in obtaining sufficient crystallized calcium *d*-gluconate (even on seeding) for his optical determinations.

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[1] *Loc. cit.*

[2] Am. Chem. J., **43**, 241.

[3] Ann. Chem. (Liebig), **357**, 227.

Strychnine d-*Arabonate.*—The crude lactone crystals, 1.03 grams, were digested in aqueous solution with an excess of strychnine until no more alkaloid dissolved and after removal of the water 3.28 grams of crude crystalline salt were obtained. This was practically insoluble in hot absolute alcohol but dissolved in a hot mixture of 9 cc. water and 60 cc. absolute alcohol. Fine feathery needles then separated out from the filtrate. They lost very little water on drying over sulphuric acid *in vacuo*, and weighed 2.3 grams after so drying. These crystals decomposed between 167° and 170° and gave $[\alpha]^{20}_{D} = -26^\circ.08$, *i. e.*, 1.055 grams salt and 24.2331 grams water gave α in a 2 dcm. tube $= -2^\circ.20$.

Quinine d-*Arabonate.*—This substance was made from 1.0 gram of the crude lactone crystals with the theoretical amount of quinine. The crude salt, 2.9 grams, dissolved in a hot solution of 3 cc. water and 30 cc. absolute alcohol, deposited a hard crust of indistinguishable crystals, 1.35 grams, melting from 172° to 173° and giving $[\alpha]^{20}_{D}$ $-106^\circ.2$; *i. e.*, 0.3589 gram substance and 8.7741 grams water gave α in a 1 dcm. tube $= -4^\circ.22$.

Brucine d-*Arabonate.*—This especially characteristic salt of

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[1] Ann. Chem. (Liebig), **357**, 267–270, 276, 281.

d-arabonic acid crystallizes from one-third its weight of water and three parts of alcohol in transparent plates melting from 167° to 170°; these lose 5.6 per cent. crystal water and become opaque on drying over sulphuric acid *in vacuo*, but the melting point remains unchanged. The specific rotation was found to be —26°.33, *i. e.*, 1.0555 grams salt and 25.3245 grams water gave α in a 2 dcm. tube = —2°.13. It is obvious from Spoehr's description of this salt[1] that it was at times contaminated with the high-melting (210°–220°) brucine salts of *dl*-glyceric, *d*-erythronic and *l*-threonic acids.

On the Constants of l-*Arabonic Lactone and its Derivatives.*—For the sake of comparison and to show more decisively, if possible, that the *d*-arabonic lactone obtained by me is the real antipode of the long-known *l*-arabonic lactone, I summarize here the various constants obtained by me and by other observers for *l*-arabonic lactone and its most characteristic derivatives. According to Nef's latest observations, 36.93 grams crude γ-*l*-arabonic lactone crystals give, when dissolved in 500 cc. hot acetone and filtered from a small amount of insoluble tar, by concentration to a small volume, 31.6 grams large, heavy, measurable, transparent crystals melting from 98° to 101° and possessing $[\alpha]_D^{20}$ —72°.2, *i. e.*, 0.4964 gram substance and 11.9138 grams water gave α in a 1 dcm. tube —2°.92. The specific rotation of the beautifully crystallized calcium salt, $(C_5H_9O_6)_2Ca.5H_2O$, is known to be 3°.1. I have made the brucine and strychnine salts of *l*-arabonic acid in the usual manner from 0.5 gram of Nef's purest γ-lactone (see above). The well-dried brucine salt melted at 160° and the strychnine salt at 117° (air dried) and 164° after drying *in vacuo*. Nef[2] gives the melting point of the vacuum-dried *l*-arabonic brucine as 155° and its specific rotation he has found to be —21°.74 (p = 4.0); the melting point of the air-dried strychnine salt was between 125° and 130°, and its specific rotation he has determined as —19°.1 (p = 4). The specific rotation of the phenylhydrazide has been determined by Nef as 14°.94 in two per cent. concentration (see above).

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[1] Am. Chem. J., **43**, 239.

[2] Nef: Ann. Chem. (Liebig), **357**, 227.

On the Unidentified Lactone Gums Obtained from the 72.15 Grams Crude d-*Arabonic Phenylhydrazide.*—As mentioned above, 9 grams of gummy lactones, $[\alpha]_D^{20}$ 52°.08, were obtained, besides 23.18 grams crude crystallized *d*-arabonic lactone, from 34 grams crude lactone gums. These were digested with 22 grams brucine, the heating being continued—as was customary—for one hour after the alkaloid had been dissolved. The cold aqueous solution was extracted three times with benzene and 35 grams of a crystalline residue obtained after removal of the water by distillation at reduced pressure. This residue, dissolved in a mixture of 10 cc. water and 160 cc. of absolute alcohol, deposited on standing 15.70 grams of crystals melting at 165° and possessing the characteristic appearance of *d*-arabonic brucine. The mother liquor then gave 15.7 grams crystalline brucine salts on distillation which, digested with 800 cc. absolute alcohol, left 0.95 gram insoluble salt melting at 195°. This may have been brucine *d*-mannonate, but I was unable to prove it by experiment. Furthermore, I was unable to establish the nature of the 14.75 grams salts dissolved by the 800 cc. absolute alcohol; I tried, for instance, to prove the presence of *d*-gluconic acid therein by conversion into the cinchonine salts, but without success. Since Nef has obtained small quantities of *l*-ribonic acid, as well as much *l*-arabonic acid, by the action of Fehling's solution on *l*-arabinose,[1] it is extremely probable that *d*-ribonic acid, whose antipode gives no well-defined alkaloid derivatives, was mainly present.

d-*Erythronic Lactone,* l-*Threonic Phenylhydrazide and* dl-*Glyceric Acid from the 19 Grams Optically Inactive Gums.*—The 19 grams inactive gums obtained by the hydrolysis of the 45 grams alcohol-soluble gummy hydrazides were digested in aqueous solution with 65 grams of brucine and then extracted as usual with benzene. Eighty-two grams of crystalline salts were left in the distilling flask after the removal of the water. These were dissolved in a hot mixture of 41 cc. water and 205 cc. of absolute alcohol and 15 grams of practically pure brucine *d*-erythronate melting at 209° separated out in plates on standing overnight. On crystallizing these from one-half a part of water and five parts of alcohol, 12.98 grams of thick crystal plates melting from 212° to 214° and possessing $[\alpha]_{\mathrm{D}}^{20}$ —25°.62 separated out. Ruff gives $[\alpha]_{\mathrm{D}}^{20}$ —23°.5 as the specific rotation of absolutely pure brucine *d*-erythronate.

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[1] Ann. Chem. (Liebig), **357**, 231.

γ-d-*Erythronic Lactone.*—On treating the 12.98 grams salts in aqueous solution with one and one-half times the calculated amount of hot aqueous barium hydroxide, filtering off the brucine and removing traces left in the alkaline solution by five-fold extraction with benzene, etc., 2.5 grams of lactone gum was obtained which solidified almost entirely on cooling. Since the sticky residue gave $[\alpha]_{\mathrm{D}}^{20}$ —71°.0, practically pure γ-d-erythronic lactone must have been present. The substance was therefore dissolved in hot ethyl acetate and on concentration to a small volume, 1.82 grams of the pure lactone was obtained in colorless prisms melting from 102° to 103° and possessing $[\alpha]_{\mathrm{D}}^{20}$ —73°.11, *i. e.*, 0.299 gram substance and 6.99 grams water gave α in a 1 dcm. tube = —3°.03. Ruff[1] gives —73°.3 as the specific rotation in 8 per cent. concentration and 103° as the melting point of this lactone. The amount of 0.1 N sodium hydroxide necessary for the neutralization of 0.4028 gram of this lactone was 33.3 cc. instead of 34.14, which is the amount demanded theoretically by $C_4H_6O_4$.

0.1792 gram of the lactone gave 0.0791 gram H_2O and 0.2661 gram CO_2.

	Calculated for $C_4H_6O_4$	Found
C	40.68	40.50
H	5.12	4.94

d-*Erythronic Phenylhydrazide.*—The 0.299 gram lactone used in the above-mentioned determination of specific rotation was treated in the customary manner with 0.3 cc. phenylhydrazine and alcohol. Owing to its great solubility only 0.3 gram phenylhydrazide melting from 119° to 120° was obtained. On crystallizing from a small amount of hot ethyl acetate 0.15 gram crystals melting at 125° and giving $[\alpha]_{\mathrm{D}}^{20}$ 17°.10 was obtained, *i. e.*, 0.145 gram substance and 3.435 grams water gave α in a 0.5 dcm. tube = 0°.35. Ruff[1] gives the melting point as 128° and the specific rotation as 17°.5.

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[1] Ber. d. chem. Ges., **32**, 3679–80.

Strychnine d-*Erythronate*.—Recent experiments by Nef and myself have proved that *d*-erythronic and *l*-threonic acids give especially beautiful, well-crystallized and very difficultly alcohol-soluble salts; these, however, can not be used as a means of separating these acids from glycollic and *dl*-glyceric acids because of the formation of mixed crystals (see below).

Pure strychnine *d*-erythronate was made from 0.5 gram of pure *d*-erythronic lactone by digestion in aqueous solution with an excess of powdered strychnine. As the crude salt, 1.9 gram, was found to dissolve with the greatest difficulty in hot absolute alcohol, it was crystallized from 2 cc. water and 10 cc. absolute alcohol; there separated out on standing overnight 0.9 gram of radiating needles melting from 198° to 199° and possessing $[\alpha]^{20}_{\mathrm{D}}$ —16°.84, *i. e.*, 0.2912 gram salt and 6.8933 grams water gave α in a 1 dcm. tube = —0°.69.

Quinine d-*Erythronate*.—The pure lactone, 0.5 gram, and the theoretical amount of quinine gave 1.95 grams crude salt. This, dissolved in 20 cc. hot absolute alcohol, gave a crop of long radiating hair-like needles weighing 0.8 gram and melting at 166° with $[\alpha]^{20}_{\mathrm{D}}$ —106°.9; *i. e.*, 0.3384 gram salt and 7.9726 grams water gave α in a 1 dcm. tube = —44°.4.

l-*Threonic Phenylhydrazide*.—The alcoholic filtrate from the 15 grams crude brucine *d*-erythronate mentioned above still contained 61 grams brucine salts which, digested with 400 cc. absolute alcohol and allowed to stand overnight, yielded 29.6 grams insoluble salts melting at 197°. After several crystallizations of this fraction from one part water and ten parts absolute alcohol, 4.93 grams salts melting at 210° and possessing $[\alpha]^{20}_{\mathrm{D}}$ —27.23° were obtained. These gave 0.9 gram lactone gum, $[\alpha]^{20}_{\mathrm{D}}$ —33°.89, which yielded on the customary treatment with phenylhydrazine 0.37 gram (in two crops) crude *l*-threonic phenylhydrazide melting at 155° and giving $[\alpha]^{20}_{\mathrm{D}}$ —25°.18. Since *l*-threonic phenylhydrazide, according to Anderson,[2] melts at 158°, crystallizes in transparent plates and possesses $[\alpha]_D^{20}$ —31°.17 (Nef found $[\alpha]_D^{20}$ —28°.78 in two independent determinations), it is obvious that *l*-threonic acid is also an oxidation product of *d*-glucose by alkaline hydrogen peroxide, but it is formed in decidedly smaller amounts than its isomer, *d*-erythronic acid. In this connection it is interesting to note that *d*-galactose, when oxidized in alkaline solution by air, hydrogen peroxide, or Fehling's solution, gives, according to Nef's latest observations, relatively far larger amounts of *l*-threonic acid than of *d*-erythronic acid. This can be understood *only* on the assumption that the methylenenol of *d*-erythrose and *l*-threose which must be formed respectively by the dissociation of 2,3-*d*-glucosedienol,

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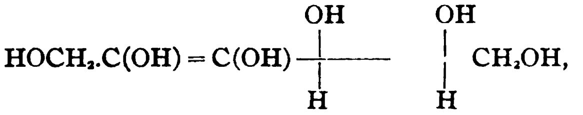
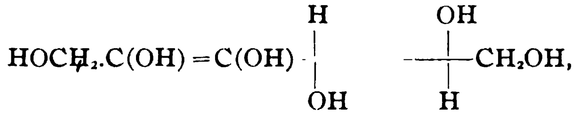
[1] *Loc. cit.*

[2] Am. Chem. J., **43**, 424.



$$HOCH_2.C(OH)=C(OH)\underset{H}{\overset{OH}{-\!\!|\!\!-}}\!\!-\!\!-\!\!-\quad\underset{H}{\overset{OH}{|}}\;CH_2OH,$$

and of 2,3-*d*-galactosedienol,



$$HOCH_2.C(OH)=C(OH)\underset{OH}{\overset{H}{|}}\quad -\!\!-\!\!\underset{H}{\overset{OH}{-\!\!|\!\!-}}CH_2OH,$$

must in each case mainly take up oxygen directly, *i. e.*, before being transformed into ordinary *d*-erythrose and *l*-threose.

dl-*Glyceric Acid.*—On setting free the acids from the brucine salts still left in the alcoholic filtrates, 45 grams by actual determination, by means of barium hydroxide, etc., 9.0 grams of gum, $[\alpha]_D^{20}$ 16°.67, were recovered. This shows very clearly that a large amount of *d*-arabonic acid must still have been present in the above-mentioned 19 grams of inactive gums obtained from the hydrolysis of the gummy alcohol-soluble phenylhydrazide. The 9 grams of gum were accordingly extracted with half a liter of hot ether and a resolution into 1.86 grams soluble gum, $[\alpha]_D^{20}$ 3°.76, and 6 grams insoluble gum, $[\alpha]_D^{20}$ 21°.66, was thereby effected. The usual treatment of the 6 grams gum with phenylhydrazine removed 1.25 grams *d*-arabonic phenylhydrazide, melting at 195° to 200°. Hydrolysis of the alcohol-soluble hydrazides—including those obtained in treating the above-mentioned 0.9 gram crude *l*-threonic gum, $[\alpha]_D^{20}$ —33°.89, with phenylhydrazine—gave back 3.96 grams acid gums, $[\alpha]_D^{20}$ 2°.5, which were therefore combined with the 1.86 grams of above-mentioned ether-soluble gums. These gave with brucine, etc., a total of 6.33 grams of high-melting (209°–214°) brucine salts which on hydrolysis gave 1.35 grams gum, $[\alpha]_D^{20}$ —10°.6. The C_4 gums—mainly *d*-erythronic—present in this gum were now removed by conversion into strychnine salts; 0.55 gram salts melting at 190° separated out on seeding and long standing. The alcoholic filtrate then gave back by barium hydroxide, etc., 1.25 grams gum, $[\alpha]_D^{20}$ 4°.4. The acid gums obtained from the 6.33 grams high-melting brucine salts by means of barium hydroxide, etc., weighed 2.77 grams and gave $[\alpha]_D^{20}$ 13°.7. Various attempts were made to resolve this gummy mixture by means of solvents (ethyl acetate) and alkaloids (strychnine) but without success, so that finally the recovered gums, about 1.75 grams, were united with the 1.25 grams gum, $[\alpha]_D^{20}$ 4°.4, which had given high-melting brucine salts (see above). The presence of a fair amount of *dl*-glyceric acid in this mixture was now unquestionably established by conversion of the combined gum, 3 grams, by digestion with quinine, subsequent extraction of the aqueous solution with ether to remove excess of alkaloid, and crystallization of the salts obtained, 12.15 grams, from water. A total of 3.7 grams of the very difficultly water-soluble quinine[1] *l*-glycerate, melting at 176°, separated out (in two crops) from the aqueous solution on standing. Over half of the total quinine salts obtained must therefore have consisted of quinine *dl*-glycerate.

II. On the Oxidation of d-*Glucose in Alkaline Solution by Air*

Fifty grams of *d*-glucose in a small amount of water were added to a cold solution of 68 grams of 98 per cent. sodium hydroxide (six equivalents) in 5 liters of water. A rapid stream of air was at once started through the solution by means of four tubes, each drawn out into six capillaries arranged in a starfish form. This enabled the air bubbles—which were first drawn through two sets of two concentrated aqueous potassium hydroxide solutions connected by two Y-tubes with the four entrance tubes—to become scattered through the whole solution. Two powerful water pumps were necessary and the air stream was continued night and day for 46 hours. The temperature of the large water bath surrounding the round-bottom six-liter flask containing the sugar solution varied between 30° and 40°. No trace of sugar was found in the perfectly colorless alkaline solution at the end of the experiment. The exact amount of hydrogen chloride necessary to neutralize the sodium hydroxide used was now added and the water and formic acid were then removed by distillation under 20 mm. pressure, taking care to sweep over all the formic acid by redissolving in water, etc.

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[1] Am. Chem. J., **42**, 421.

Determination of the Formic Acid.—The total amount of aqueous distillate, giving a barely perceptible opalescence with silver nitrate, was 5355 cc. One hundred cc. of this required 46.1 cc. 0.0999 N potassium hydroxide for neutralization (phenolphthalein), which is equivalent to 0.2118 gram formic acid; hence the total amount of formic acid formed from 50 grams *d*-glucose was 11.35 grams (14.8 per cent.).

The Nonvolatile Gummy Acids.—The residue in the distilling flask was now treated in aqueous solution with 160 cc. concentrated (36 per cent.) hydrochloric acid in order to insure the complete liberation of all organic acids. The residual gums, smelling therefore strongly of hydrochloric acid, were freed from sodium chloride in the usual manner; 36 grams of lactone gums, giving $[\alpha]_D^{20}$ 22°.98, and still containing small amounts of sodium chloride, were finally obtained, which shows that the yield of nonvolatile hydroxy acids is enormous when compared with the corresponding experiment with hydrogen peroxide. The gum was now resolved by digestion with half a liter of ethyl acetate into a soluble fraction, 26 g.; and an insoluble portion which, when freed from a small amount of sodium chloride by means of absolute alcohol, weighed 11 grams—gum *C*—and gave $[\alpha]_D^{20}$ 34°.27.

The soluble fraction was further resolved by thorough extraction with ether—four times with a half liter each time—into 12.8 grams ether-soluble gums, *A*, with $[\alpha]_D^{20}$ 10°.70, and into 12.2 grams ether-insoluble gums, B, with $[\alpha]_D^{20}$ 36°.48. Gums B and C were now treated in the usual manner with phenylhydrazine and absolute alcohol; the former gave 8.25 grams phenylhydrazides melting at 210° and the latter gave 5.7 grams of similar crystals melting at 193°. These two crops were therefore united and worked up for *d*-arabonic lactone after adding 1.9 grams hydrazides, melting at 195°, subsequently obtained from the combined alcoholic filtrates by distilling off the alcohol *in vacuo*, dissolving in water, extracting with ether, etc. The gummy alcohol-soluble phenylhydrazides, 18 grams, then gave back on the usual hydrolysis with barium hydroxide, etc., 10 grams lactone gums, $[\alpha]_D^{20}$ 5°.75.

γ-d-*Arabonic Lactone.*—Hydrolysis of the combined high melting phenylhydrazides, 15.85 grams, by barium hydroxide now gave 8.0 grams of crude *d*-arabonic lactone gums. I succeeded in obtaining from these by extraction with ethyl acetate, digestion with water, etc., as described in Part I, 4.49 grams of crystallized γ-*d*-arabonic lactone giving $[\alpha]_D^{20}$ 67°.70, *i. e.*, 0.6093 gram lactone and 14.5007 gram water gave α in a 1 dcm. tube = 2°.76.

The total amount of the noncrystallizable lactone gums found in the filtrates was 3.0 grams; from these I obtained by conversion into brucine salts and subsequent crystallization only 3.3 grams of transparent crystalline plates melting from 167° to 170° and obviously consisting of brucine *d*-arabonate. It is, however, possible in this case also that a small amount of *d*-mannonic as well as of *d*-gluconic acid, and especially also some *d*-ribonic acid, was present, but I was unable to prove this by experiment.

d-*Erythronic Lactone and* dl-*Glyceric Acid.*—The A gums, 12.8 grams, $[\alpha]_D^{20}$ 10°.7, and the 10 grams gums $[\alpha]_D^{20}$ 5°.75, obtained from the alcohol-soluble gummy hydrazides from the B and C gums, obviously still contained a fair amount of *d*-arabonic lactone. I found first that it was possible to effect a considerable resolution of this gummy mixture by dissolving the gums partially in ten parts of hot acetic ester and then extracting the soluble portion with one hundred parts of hot ether. The ten-gram portion, for instance, was thus resolved into three fractions: 3.0 grams, $[\alpha]_D^{20}$ —1°.6; 1.5 grams, $[\alpha]_D^{20}$ 6°.0; and 5.0 grams, $[\alpha]_D^{20}$ 11°.2, arranged in the order of solubility. Similarly, 9.5 grams of gum, $[\alpha]_D^{20}$ 10°.5, was resolved by digestion with half a liter of ether into 1.5 grams optically inactive soluble gums, and into 6.5 grams insoluble gums, $[\alpha]_D^{20}$ 18°.49; the latter then gave with phenylhydrazine 1.35 grams more *d*-arabonic phenylhydrazide, melting at 195° to 210°. Furthermore, I also tried conversion of the various gums into brucine salts in the hope of being able to accomplish a sharp separation of the high-melting (210° to 220°) brucine salts of *d*-erythronic, *dl*-glyceric and *l*-threonic acids from brucine *d*-arabonate which melts at 167° to 170°. I was unsuccessful in this, as I obtained large amounts of mixed crystals of these various salts, melting in the neighborhood of 180° to 200°. It was therefore with very great difficulty, and after many recrystallizations, that I finally obtained from the above-mentioned 22.8 grams of unidentified gums a total of 9.87 grams crude brucine *d*-arabonate melting from 150° to 170°, and 21.29 grams brucine salts melting from 208° to 214°. The latter then gave on treatment with barium hydroxide 4.15 grams lactone gum, $[\alpha]_D^{20}$ —10°.0, which on treatment with excess of strychnine took up 10.35 grams of this alkaloid. On distilling there was obtained a crystalline residue weighing 16 grams which gave two crops of salts on crystallization from spirit; 2.86 grams melting at 180° to 198°, with $[\alpha]_D^{20}$ —19°.43, and 2.38 grams melting at 130° to 150°, with $[\alpha]_D^{20}$ —18°.85. The former gave 0.8 gram lactone, $[\alpha]_D^{20}$ —44°.37, and the latter gave 0.57 gram gum, $[\alpha]_D^{20}$ 1°.7, which shows therefore the presence of small amounts of *d*-arabonic lactone.

The 0.8 gram gum, $[\alpha]_D^{20}$ —44°.37, solidified on cooling and gave, on crystallizing from a small amount of ethyl acetate, 0.3 gram of crude *d*-erythronic lactone, melting at 95°, and possessing $[\alpha]_D^{20}$ —66°.79, *i. e.*, 0.1085 gram lactone and 3.0495 grams water gave α in a 0.5 dcm. tube = —1°.16.

The 0.57 gram gum, $[\alpha]_D^{20}$ 1°.7, obtained from the second crop of strychnine salts, contained *dl*-glyceric acid mainly, for it gave on conversion into its quinine salt (1.74 grams obtained) a crop of 0.5 gram of quinine *l*-glycerate melting at 175° on crystallizing the salt from water.

Finally two other slightly active gums—2.95 grams, $[\alpha]_D^{20}$ 5°.7, and 2.33 grams, $[\alpha]_D^{20}$ 0°.86, the latter having been obtained from the alcohol-soluble strychnine salts from the above 4.15 grams lactone gum, $[\alpha]_D^{20}$ —10°.0—were converted into quinine salts. These gums took up 16 grams quinine and gave a crystalline residue of 25 grams. This residue gave on crystallization from water a total of 6.1 grams quinine *l*-glycerate melting at 174°, which proves very clearly that *dl*-glyceric acid was the main component of these gums. It is also clear from the above data that the separation of *dl*-glyceric acid from the two C_4 acids, *d*-erythronic and *l*-threonic, by means of strychnine, is not sharp but that mixed crystals of all of these components separate out from absolute alcohol. I have proved in an independent experiment that pure *dl*-glyceric acid gives with strychnine a low-melting (112° to 125°) crystalline salt which comes out to a very limited extent only from absolute alcohol, in which it is very soluble.

In conclusion, attention is drawn to the fact that I succeeded in proving definitely the nature of a far smaller proportion of the nonvolatile hydroxy acids formed by the action of air on an alkaline solution of *d*-glucose as compared with hydrogen peroxide. This is due mainly to the fact that in the former case relatively far greater amounts of *dl*-glyceric and optically active trihydroxybutyric acids are formed in proportion to the *d*-arabonic acid. I succeeded, for example, in obtaining only 17.75 grams of crude *d*-arabonic phenylhydrazide from 36 grams gums in the case of air, whereas I obtained 72.15 grams similar hydrazides from 83 grams of nonvolatile gums in the hydrogen peroxide experiment. The specific rotation of the original nonvolatile hydroxy acids was therefore also found to be far more strongly dextro in the latter case. Furthermore, experience has shown that it is impossible to remove more than a very small amount of *d*-arabonic lactone by the phenylhydrazine treatment of gummy mixtures whose specific rotation is not greater than 30°.0. It would therefore have been far more advantageous had I first resolved my gummy lactone mixtures, whose specific rotations varied from 5° to 30°, by digestion with solvents (small quantities of ethyl acetate and subsequently much ether, etc.) into gummy fractions which were levorotatory and into dextrorotatory gums whose specific rotation was at least 40°, before further treatment with reagents.

To Dr. Nef, whose constant help alone made this work possible, I extend my heartiest thanks.